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(54) Title: LIQUID DISHWASHING DETERGENTS CONTAINING SUDS STABILIZERS

(57) Abstract

The present invention relates to proteinaceous suds stabilizers suitable for use in liquid detergent compositions, said proteinaceous suds stabilizers provide enhanced suds volume and suds retention thereby signaling the lasting efficacy of the detersive ingredients. The proteinaceous suds stabilizers may be naturally occurring polypeptide polymers, for example, enzymes, or synthetic amino acid containing polymers. The proteinaceous suds stabilizers are further identified in that they have an isoelectric point of from about 7 to about 11.5.

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LIQUID DISHWASHING DETERGENTS CONTAINING SUDS STABILIZERS

FIELD OF THE INVENTION

The present invention relates to liquid detergent compositions useful for hand dishwashing, said compositions comprising a proteinaceous suds stabilizer which provides increased grease removal performance and increased duration of sudzing. The effective proteinaceous suds stabilizers of the present invention have an isoelectric point of from about 9 to about 11.5. The present invention also relates to amino acid or amino acid-like containing proteinaceous materials which provide a polymeric material having an isoelectric point of from about 9 to about 11.5.

BACKGROUND OF THE INVENTION

Liquid detergent compositions which are suitable for hand dishwashing must satisfy several criteria in order to be effective. These compositions must be effective in cutting grease and greasy food material and once removed, must keep the greasy material from re-depositing on the dishware.

The presence of suds in a hand dishwashing operation has long been used as a signal that the detergent continues to be effective. However, depending upon the circumstances, the presence of suds or the lack thereof, has no bearing upon the efficacy of liquid detergents. Therefore, the consumer has come to rely upon a somewhat erroneous signal, the lack or absence of soap suds, to indicate the need for additional detergent. In many instances the consumer is adding an additional amount of detergent far in excess of the amount necessary to thoroughly clean the dishes. This wasteful use of detergent is especially true in hand dishwashing since the soiled cooking articles are usually cleaned in a "washing difficulty" queue, for example, glasses and cups, which usually do not contact greasy food, are washed first, followed by plates and flatware, and finally pots and pans which contain the most residual food material and are usually, therefore, the "greasiest".

The lack of suds in the dishwater when pots and pans are usually cleaned, together with the visual inspection of the amount of residual food material on the cookware surface, typically compels the consumer to add additional detergent when a sufficient amount still remains in solution to effectively remove the soil and grease from the dishware or cookware surface. However, effective grease cutting materials do not necessarily produce a substantial amount of corresponding suds.

Accordingly, there remains a need in the art for liquid dishwashing detergents useful for hand washing dishware which have an enduring suds level while maintaining effective grease cutting properties. The need exists for a composition which can

maintain a high level of suds as long as the dishwashing composition is effective. Indeed, there is a long felt need to provide a hand dishwashing composition which can be use efficiently by the consumer such that the consumer uses only the necessary amount of detergent to fully accomplish the cleaning task.

SUMMARY OF THE INVENTION

The present invention meets the aforementioned needs in that it has been surprisingly discovered that certain proteinaceous compounds serve as suds extenders in liquid detergent compositions which are effective in cutting grease. The effective proteinaceous suds stabilizers have an isoelectric point of from about 9 to about 11.5 and are effective in liquid detergent compositions which have a pH of from about 7 to about 12 when measured as a 10% aqueous solution.

The proteinaceous suds stabilizers of the present invention comprise at least about 10% by weight of one or more amino acid residues, preferably amino acid residues having a proton accepting or proton donor moiety. The proteinaceous suds stabilizers can comprise any other amino acid compatible units which provide for extended suds formation and suds volume.

A first aspect of the present invention relates to detergent compositions suitable for use in hand dishwashing, said compositions comprising:

a) an effective amount of a proteinaceous suds stabilizer, said stabilizer having an isoelectric point of from about 9 to about 11.5;

b) an effective amount of a detersive surfactant; and

c) the balance carriers and other adjunct ingredients;

provided the pH of a 10% aqueous solution of said composition is from about 7 to about 12.

The present invention further relates to proteinaceous materials in the form of peptides, polypeptides, peptide copolymers, and mixtures thereof which are suitable for use in detergents wherein the formulator desires to extend the amount and duration of suds.

The present invention also relates to methods for providing increased suds and increased duration of suds while hand washing dishware comprising the step of dissolving a composition according to the present invention in water to form a hand dish washing solution and then washing dishware by hand in said solution. These and other aspects, features and advantages will become apparent to those of ordinary skill in the art from a reading of the following detailed description and the appended claims.

All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius (^{o} C) unless otherwise specified. All documents cited are in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to peptides, polypeptides, amino acid containing copolymers, and the like which provide suds stability and enhancement of suds duration during hand washing of dishware. The present invention also relates to liquid detergent compositions comprising said proteinaceous suds stabilizers which provide extended suds benefits.

Proteinaceous Suds Stabilizers

The proteinaceous suds stabilizers of the present invention can be peptides, polypeptides, amino acid containing copolymers, and mixtures thereof. Any suitable amino acid can be used to form the backbone of the peptides, polypeptides, or amino acid containing copolymers of the present invention provided at least 10% to about 40% of said amino acids which comprise the peptides are capable of being protonated at a pH of from 7 to about 11.5.

For the purposes of the present invention the term "peptide" and "polypeptide" stand equally well for polymers which comprise 100% amino acids as described herein below and which have a molecular weight of at least about 1500 daltons. For the purposes of the present invention the term "amino acid containing co-polymers" is defined as "polymeric material comprising at least about 10% by weight of one or more amino acids as defined herein provided said polymeric material has a molecular weight of at least about 1500 daltons".

The preferred proteinaceous suds stabilizers according to the present invention have an isoelectric point of form 7 to about 11.5, preferably from about 8.5 to about 11.5, more preferably form about 9.5 to about 11.

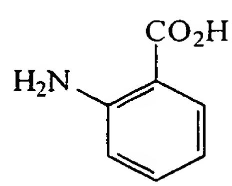
In general, the amino acids suitable for use in forming the proteinaceous suds stabilizers of the present invention have from 2 to 22 carbon atoms, said amino acids having the formula:

$$H_2N — \underset{R^2}{\overset{R^2}{(C)}}_x — \underset{R^1}{\overset{R}{C}} — \underset{R^2}{\overset{R^2}{(C)}}_y — \overset{O}{\overset{\|}{C}} — OH$$

wherein R and R^1 are each independently hydrogen, C_1-C_6 linear or branched alkyl, C_1-C_6 substituted alkyl, and mixtures thereof. Non-limiting examples of suitable moieties

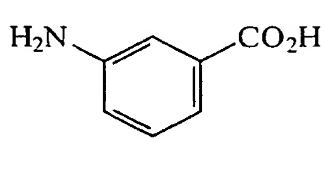
for substitution on the C_1-C_6 alkyl units include amino, hydroxy, carboxy, amido, thio, thioalkyl, phenyl, substituted phenyl, wherein said phenyl substitution is hydroxy, halogen, amino, carboxy, amido, and mixtures thereof. Further non-limiting examples of suitable moieties for substitution on the R and R^1 C_1-C_6 alkyl units include 3-imidazolyl, 4-imidazolyl, 2-imidazolinyl, 4-imidazolinyl, 2-piperidinyl, 3-piperidinyl, 4-piperidinyl, 1-pyrazolyl, 3-pyrazoyl, 4-pyrazoyl, 5-pyrazoyl, 1-pyrazolinyl, 3-pyrazolinyl, 4-pyrazolinyl, 5-pyrazolinyl, 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, piperazinyl, 2-pyrrolidinyl, 3-pyrrolidinyl, guanidino, amidino, and mixtures thereof. Preferably R^1 is hydrogen and at least 10% of R units are moieties which are capable of having a positive or negative charge at a pH of from about 7 to about 11.5. Each R^2 is independently hydrogen, hydroxy, amino, guanidino, C_1-C_4 alkyl, or comprises a carbon chain which can be taken together with R, R^1 any R^2 units to form an aromatic or non-aromatic ring having from 5 to 10 carbon atoms wherein said ring may be a single ring or two fused rings, each ring being aromatic, non-aromatic, or mixtures thereof. When the amino acids according to the present invention comprise one or more rings incorporated into the amino acid backbone, then R, R^1, and one or more R^2 units will provide the necessary carbon-carbon bonds to accommodate the formation of said ring. Preferably when R is hydrogen, R^1 is not hydrogen, and vice versa; preferably at least one R^2 is hydrogen. The indices x and y are each independently from 0 to 2.

An example of an amino acid according to the present invention which contains a ring as part of the amino acid backbone is 2-aminobenzoic acid (anthranilic acid) having the formula:



wherein x is equal to 1, y is equal to 0 and R, R^1, and 2 R^2 units from the same carbon atom are taken together to form a benzene ring.

A further example of an amino acid according to the present invention which contains a ring as part of the amino acid backbone is 3-aminobenzoic acid having the formula:



wherein x and y are each equal to 1, R is hydrogen and R^1 and four R^2 units are taken together to form a benzene ring.

Non-limiting examples of amino acids suitable for use in the proteinaceous suds stabilizers of the present invention wherein at least one x or y is not equal to 0 include 2-aminobenzoic acid, 3-aminobenzoic acid, 4-aminobenzoic acid, β-alanine, and β-hydroxyaminobutyric acid.

The preferred amino acids suitable for use in the proteinaceous suds stabilizers of the present invention have the formula:

$$H_2N\text{—}(CH_2)_x\text{—}\underset{R^1}{\overset{R}{\overset{|}{\underset{|}{C}}}}\text{—}(CH_2)_y\text{—}\overset{O}{\overset{\|}{C}}\text{—}OH$$

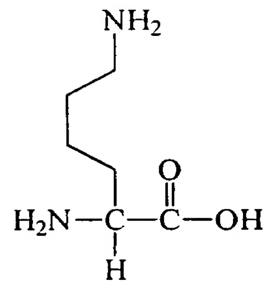
wherein R and R^1 are independently hydrogen or a moiety as describe herein above preferably R^1 is hydrogen and at least from about 10% to about 40% of R units comprise a moiety having a positive charge at a pH of from about 7 to about 11.5.

More preferred amino acids which comprise the proteinaceous suds stabilizers of the present invention have the formula:

$$H_2N\text{—}\underset{H}{\overset{R}{\overset{|}{\underset{|}{C}}}}\text{—}\overset{O}{\overset{\|}{C}}\text{—}OH$$

wherein R is hydrogen, C_1-C_6 linear or branched alkyl, C_1-C_6 substituted alkyl, and mixtures thereof. R is preferably C_1-C_6 substituted alkyl wherein preferred moieties which are substituted on said C_1-C_6 alkyl units include amino, hydroxy, carboxy, amido, thio, C_1-C_4 thioalkyl, 3-imidazolyl, 4-imidazolyl, 2-imidazolinyl, 4-imidazolinyl, 2-piperidinyl, 3-piperidinyl, 4-piperidinyl, 1-pyrazolyl, 3-pyrazoyl, 4-pyrazoyl, 5-pyrazoyl, 1-pyrazolinyl, 3-pyrazolinyl, 4-pyrazolinyl, 5-pyrazolinyl, 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, piperazinyl, 2-pyrrolidinyl, 3-pyrrolidinyl, guanidino, amidino, phenyl, substituted phenyl, wherein said phenyl substitution is hydroxy, halogen, amino, carboxy, and amido.

An example of a more preferred amino acid according to the present invention is the amino acid lysine having the formula:



wherein R is a substituted C_1 alkyl moiety, said substituent is 4-imidazolyl.

Non-limiting examples of preferred amino acids include alanine, arginine, asparagine, aspartic acid, cysteine, glutamine, glutamic acid, glycine, histidine, isoleucine, leucine, lysine, methionine, phenylalanine, proline, serine, threonine, tryptophan, tyrosine, valine, and mixtures thereof. The aforementioned amino acids are typically referred to as the "primary α-amino acids", however, the proteinaceous suds stabilizers of the present invention may comprise any amino acid having an R unit which together with the aforementioned amino acids serves to adjust the isoelectric point of the proteinaceous suds stabilizers to a range of from about 7 to about 11.5. For example, further non-limiting examples of amino acids include homoserine, hydroxyproline, norleucine, norvaline, ornithine, penicillamine, and phenylglycine, preferably ornithine. R units preferably comprise moieties which are capable of a cationic or anionic charges within the range of pH from about 7 to about 11.5. Non-limiting examples of preferred amino acids having anionic R units include glutamic acid, aspartic acid, and γ-carboxyglutamic acid.

For the purposes of the present invention, both optical isomers of any amino acid having a chiral center serve equally well for inclusion into the backbone of the peptide, polypeptide, or amino acid copolymers. Racemic mixtures of one amino acid may be suitably combined with a single optical isomer of one or more other amino acids depending upon the desired properties of the final proteinaceous suds stabilizer. The same applies to amino acids capable of forming diasteriomeric pairs, for example, threonine.

1. <u>Polyamino Acid Proteinaceous Suds Stabilizer</u>

One type of suitable proteinaceous suds stabilizer according to the present invention is comprised entirely of the amino acids described herein above. Said polyamino acid compounds may be naturally occurring peptides, polypeptides, enzymes, and the like, provided said compounds have an isoelectric point of from about 7 to about 11.5 and a molecular weight greater than or equal to about 1500 daltons. Preferably the proteinaceous suds stabilizers of the present invention which are comprised entirely of

amino acids, comprise from about 10% to about 40% by weight, of amino acids which are capable of being protonated at a pH of from about 7 to about 11.5. An example of a polyamino acid which is suitable as a proteinaceous suds stabilizer according to the present invention is the enzyme lysozyme.

An exception may, from time to time, occur in the case where naturally occurring enzymes, proteins, and peptides are chosen as proteinaceous suds stabilizers. Without wishing to be limited by theory, the unique secondary, tertiary, or quaternary structure of said naturally occurring polypeptides may permit their use even though the amount of protonatable amino acids within the pH range of from about 7 to about 11.5 is outside the range of from about 10% to about 40% by weight. For example an enzyme having an isoelectric point in the range of from about 7 to about 11.5 which only comprises 5% by weight amino acids having R units which are protonated at a pH of from about 7 to about 11.5 may suitably serve as an effective proteinaceous suds stabilizer according to the present invention.

Another class of suitable polyamino acid compound is the synthetic peptide having a molecular weight of at least about 1500 daltons and further comprising from about 10% to about 40% by weight of amino acids capable of being protonated at a pH of form about 7 to about 11.5. In addition, said polyamino acid peptides must have an isoelectric point of form 7 to about 11.5, preferably from about 8.5 to about 11.5, more preferably form about 9.5 to about 11. An example of a polyamino acid synthetic peptide suitable for use as a proteinaceous suds stabilizer according to the present invention is the copolymer of the amino acids lysine, alanine, glutamic acid, and tyrosine having an average molecular weight of 52,000 daltons and a ratio of lys:ala:glu:tyr of approximately 5:6:2:1.

Without wishing to be limited by theory, the presence of one or more cationic amino acids, for example, histidine, ornithine, lysine and the like, is required to insure increased suds stabilization and suds volume. However, the relative amount of cationic amino acid present, as well as the resulting isoelectric point of the polyamino acid, are key to the effectiveness of the resulting material. For example, poly L-lysine having a molecular weight of approximately 18,000 daltons comprises 100% amino acids which have the capacity to possess a positive charge in the pH range of from about 7 to about 11.5, with the result that this material is ineffective as a suds extender and as a greasy soil removing agent.

2. Peptide Copolymers

Another class of materials suitable for use as proteinaceous suds stabilizers according to the present invention are peptide copolymers. For the purposes of the

present invention "peptide copolymers" are defined as "polymeric materials with a molecular weight greater than or equal to about 1500 daltons having an isoelectric point of from about 7 to about 11.5 wherein at least about 10% by weight of said polymeric material comprises one or more amino acids".

Peptide copolymers suitable for use as proteinaceous suds stabilizers may include segments of polyethylene oxide which are linked to segments of peptide or polypeptide to form a material which has increased suds retention as well as formulatability.

Nonlimiting examples of amino acid copolymer classes include the following.

A. Polyalkyleneimine copolymers.

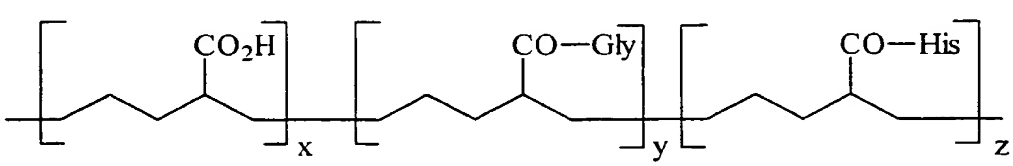
Polyalkyleneimine copolymers comprise random segments of polyalkyleneimine, preferably polyethyleneimine, together with segments of amino acid residues. For example, tetraethylenepentamine is reacted together with polyglutamic acid and polyalanine to form a copolymer having the formula:

$$\left[-[HN-R]_{n+1}-[\overset{H}{\overset{|}{N}}-R]_m-[\overset{|}{N}-R]_n-NH- \right]_x \left[-(Glu)_i- \right]_y \left[-(Ala)_j- \right]_z$$

wherein m is equal to 3, n is equal to 0, i is equal to 3, j is equal to 5, x is equal to 3, y is equal to 4, and z is equal to 7.

However, the formulator may substitute other polyamines for polyalkyleneimines, for example, polyvinyl amines, or other suitable polyamine which provides for a source of cationic charge at a pH of from 7 to abut 11.5 and which results in a copolymer having an isoelectric point of from about 7 to about 11.5.

The formulator may combine non-amine polymers with protonatable as well as non-protonatable amino acids. For example, a carboxylate-containing homo-polymer may be reacted with one or more amino acids, for example, histidine and glycine, to form an amino acid containing amido copolymer having the formula:



wherein said copolymer has a molecular weight of at least 1500 daltons and a ratio of x : y : z of approximately 2 : 3 : 6.

The liquid detergent compositions according to the present invention comprise at least an effective amount of one or more proteinaceous suds stabilizers described herein,

preferably from about 0.3% to about 5%, more preferably from about 0.4% to about 4%, most preferably from about 0.5% to about 3% by weight, of said composition. What is meant herein by "an effective amount of proteinaceous suds stabilizer" is that the suds produced by the presently described compositions are sustained for an increased amount of time relative to a composition which does not comprise a proteinaceous suds stabilizer described herein.

Detersive Surfactants

The compositions of the present invention comprise at least an effective amount of one or more detersive surfactants. The term "effective amount" is defined herein as "the amount of surfactant necessary to suitably clean a surface, preferably a tableware surface (i.e., glasses, silverware, plate, pots and pans) while the proteinaceous suds stabilizer maintains an increased level of sudsing". An effective amount is typically from about 0.5% to about 90%, preferably from about 5% to about 50%, more preferably from about 10% to about 30% by weight, of detersive surfactant.

Anionic Surfactants - The anionic surfactants useful in the present invention are preferably selected from the group consisting of, linear alkylbenzene sulfonate, α- olefin sulfonate, paraffin sulfonates, methyl ester sulfonates, alkyl sulfates, alkyl alkoxy sulfate, alkyl sulfonates, alkyl alkoxy carboxylate, alkyl alkoxylated sulfates, sarcosinates, taurinates, and mixtures thereof.

One type of anionic surfactant which can be utilized encompasses alkyl ester sulfonates. These are desirable because they can be made with renewable, non-petroleum resources. Preparation of the alkyl ester sulfonate surfactant component can be effected according to known methods disclosed in the technical literature. For instance, linear esters of C_8-C_{20} carboxylic acids can be sulfonated with gaseous SO_3 according to "The Journal of the American Oil Chemists Society," 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm, and coconut oils, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprises alkyl ester sulfonate surfactants of the structural formula:

$$R^3\text{—}\underset{\displaystyle SO_3M}{\underset{|}{CH}}\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}OR^4$$

wherein R^3 is a C_8-C_{20} hydrocarbyl, preferably an alkyl, or combination thereof, R^4 is a C_1-C_6 hydrocarbyl, preferably an alkyl, or combination thereof, and M is a soluble salt-forming cation. Suitable salts include metal salts such as sodium, potassium, and lithium

salts, and substituted or unsubstituted ammonium salts, such as methyl-, dimethyl, -trimethyl, and quaternary ammonium cations, e.g. tetramethyl-ammonium and dimethyl piperdinium, and cations derived from alkanolamines, e.g. monoethanol-amine, diethanolamine, and triethanolamine. Preferably, R^3 is C_{10}-C_{16} alkyl, and R^4 is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R^3 is C_{14}-C_{16} alkyl.

Alkyl sulfate surfactants are another type of anionic surfactant of importance for use herein. In addition to providing excellent overall cleaning ability when used in combination with polyhydroxy fatty acid amides (see below), including good grease/oil cleaning over a wide range of temperatures, wash concentrations, and wash times, dissolution of alkyl sulfates can be obtained, as well as improved formulability in liquid detergent formulations are water soluble salts or acids of the formula $ROSO_3M$ wherein R preferably is a C_{10}-C_{24} hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C_{10}-C_{20} alkyl component, more preferably a C_{12}-C_{18} alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali or alkaline (Group IA or Group IIA) metal cation (e.g., sodium, potassium, lithium, magnesium, calcium), substituted or unsubstituted ammonium cations such as methyl-, dimethyl-, and trimethyl ammonium and quaternary ammonium cations, e.g., tetramethyl-ammonium and dimethyl piperdinium, and cations derived from alkanolamines such as ethanolamine, diethanolamine, triethanolamine, and mixtures thereof, and the like. Typically, alkyl chains of C_{12-16} are preferred for lower wash temperatures (e.g., below about 50°C) and C_{16-18} alkyl chains are preferred for higher wash temperatures (e.g., above about 50°C).

Alkyl alkoxylated sulfate surfactants are another category of useful anionic surfactant. These surfactants are water soluble salts or acids typically of the formula $RO(A)_mSO_3M$ wherein R is an unsubstituted C_{10}-C_{24} alkyl or hydroxyalkyl group having a C_{10}-C_{24} alkyl component, preferably a C_{12}-C_{20} alkyl or hydroxyalkyl, more preferably C_{12}-C_{18} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations, such as tetramethyl-ammonium, dimethyl piperidinium and cations derived from alkanolamines, e.g. monoethanolamine, diethanolamine, and triethanolamine, and mixtures thereof. Exemplary surfactants are C_{12}-C_{18} alkyl polyethoxylate (1.0) sulfate, C_{12}-C_{18} alkyl

polyethoxylate (2.25) sulfate, C_{12}-C_{18} alkyl polyethoxylate (3.0) sulfate, and C_{12}-C_{18} alkyl polyethoxylate (4.0) sulfate wherein M is conveniently selected from sodium and potassium. Surfactants for use herein can be made from natural or synthetic alcohol feedstocks. Chain lengths represent average hydrocarbon distributions, including branching.

Other Anionic Surfactants - Other anionic surfactants useful for detersive purposes can also be included in the compositions hereof. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C_9-C_{20} linear alkylbenzenesulphonates, C_8-C_{22} primary or secondary alkanesulphonates, C_8-C_{24} olefinsulphonates, sulphonated polycarboxylic acids prepared by sulphonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isothionates such as the acyl isothionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C_{12}-C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_6-C_{14} diesters), N-acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, alkyl polyethoxy carboxylates such as those of the formula $RO(CH_2CH_2O)_kCH_2COO\text{-}M^+$ wherein R is a C_8-C_{22} alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation, and fatty acids esterified with isethionic acid and neutralized with sodium hydroxide. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. 3,929,678 Laughlin *et al.*, issued December 30, 1975 at Column 23, line 58 through Column 29, line 23.

Secondary Surfactants - Secondary detersive surfactant can be selected from the group consisting of nonionics, cationics, ampholytics, zwitterionics, and mixtures thereof. By selecting the type and amount of detersive surfactant, along with other adjunct ingredients disclosed herein, the present detergent compositions can be formulated to be used in the context of laundry cleaning or in other different cleaning applications, particularly including dishwashing. The particular surfactants used can

therefore vary widely depending upon the particular end-use envisioned. Suitable secondary surfactants are described below.

Nonionic Detergent Surfactants - Suitable nonionic detergent surfactants are generally disclosed in U.S. 3,929,678 Laughlin *et al.*, issued December 30, 1975, at column 13, line 14 through column 16, line 6, incorporated herein by reference. Exemplary, non-limiting classes of useful nonionic surfactants include: alkyl dialkyl amine oxide, alkyl ethoxylate, alkanoyl glucose amide, alkyl betaines, and mixtures thereof.

Other nonionic surfactants for use herein include:

The polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols. In general, the polyethylene oxide condensates are preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 12 carbon atoms in either a straight chain or branched chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 5 to about 25 moles of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include Igepal® CO-630, marketed by the GAF Corporation; and Triton® X-45, X-114, X-100, and X-102, all marketed by the Rohm & Haas Company. These compounds are commonly referred to as alkyl phenol alkoxylates, (e.g., alkyl phenol ethoxylates).

The condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from about 10 to about 20 carbon atoms with from about 2 to about 18 moles of ethylene oxide per mole of alcohol. Examples of commercially available nonionic surfactants of this type include Tergitol® 15-S-9 (the condensation product of C_{11}-C_{15} linear secondary alcohol with 9 moles ethylene oxide), Tergitol® 24-L-6 NMW (the condensation product of C_{12}-C_{14} primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol® 45-9 (the condensation product of C_{14}-C_{15} linear alcohol with 9 moles of ethylene oxide), Neodol® 23-6.5 (the condensation product of C_{12}-C_{13} linear alcohol with 6.5 moles of ethylene oxide), Neodol® 45-7 (the condensation product of C_{14}-C_{15} linear alcohol with 7 moles of ethylene oxide), Neodol® 45-4 (the condensation product of C_{14}-C_{15} linear alcohol with 4 moles of ethylene oxide), marketed by Shell Chemical Company, and Kyro® EOB (the condensation product of C_{13}-C_{15} alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble

Company. Other commercially available nonionic surfactants include Dobanol 91-8® marketed by Shell Chemical Co. and Genapol UD-080® marketed by Hoechst. This category of nonionic surfactant is referred to generally as "alkyl ethoxylates."

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of these compounds preferably has a molecular weight of from about 1500 to about 1800 and exhibits water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available Pluronic® surfactants, marketed by BASF.

The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic® compounds, marketed by BASF.

Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula:

$$R^3(OR^4)_xN(R^5)_2 \quad (N\rightarrow O)$$

wherein R^3 is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R^5 is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R^5 groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C_{10}-C_{18} alkyl dimethyl amine oxides and C_8-C_{12} alkoxy ethyl dihydroxy ethyl amine oxides.

Alkylpolysaccharides disclosed in U.S. 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside.) The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

Optionally, and less desirably, there can be a polyalkylene-oxide chain joining the hydrophobic moiety and the polysaccharide moiety. The preferred alkyleneoxide is ethylene oxide. Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from about 8 to about 18, preferably from about 10 to about 16, carbon atoms. Preferably, the alkyl group is a straight chain saturated alkyl group. The alkyl group can contain up to about 3 hydroxy groups and/or the polyalkyleneoxide chain can contain up to about 10, preferably less than 5, alkyleneoxide moieties. Suitable alkyl polysaccharides are octyl, nonyl, decyl, undecyldodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexaglucosides, galactosides, lactosides, glucoses, fructosides, fructoses and/or galactoses. Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentaglucosides and tallow alkyl tetra-, penta-, and hexa-glucosides.

The preferred alkylpolyglycosides have the formula

$$R^2O(C_nH_{2n}O)_t(\text{glycosyl})_x$$

wherein R^2 is selected from the group consisting of alkyl, alkyl-phenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominantly the 2-position.

Fatty acid amide surfactants having the formula:

$$R^6-\overset{\displaystyle O}{\overset{\|}{C}}-(NR^7)_2$$

wherein R^6 is an alkyl group containing from about 7 to about 21 (preferably from about 9 to about 17) carbon atoms and each R^7 is selected from the group consisting of hydrogen, C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, and $-(C^2H_4O)_xH$ where x varies from about 1 to about 3.

Preferred amides are C_8-C_{20} ammonia amides, monoethanolamides, diethanolamides, and isopropanolamides.

Cationic Surfactants - Cationic detersive surfactants can also be included in detergent compositions of the present invention. Cationic surfactants include the ammonium surfactants such as alkyldimethylammonium halogenides, and those surfactants having the formula:

$$[R^2(OR^3)_y][R^4(OR^3)_y]_2R^5N^+X^-$$

wherein R^2 is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R^3 is selected from the group consisting of $-CH_2CH_2-$, $-CH_2CH(CH_3)-$, $-CH_2CH(CH_2OH)-$, $-CH_2CH_2CH_2-$, and mixtures thereof; each R^4 is selected from the group consisting of C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, benzyl, ring structures formed by joining the two R^4 groups, $-CH_2CHOHCHOHCOR^6CHOH-CH_2OH$ wherein R^6 is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not O; R^5 is the same as R^4 or is an alkyl chain wherein the total number of carbon atoms of R^2 plus R^5 is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Other cationic surfactants useful herein are also described in U.S. 4,228,044, Cambre, issued October 14, 1980, incorporated herein by reference.

Other Surfactants - Ampholytic surfactants can be incorporated into the detergent compositions hereof. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate. See U.S. 3,929,678 Laughlin *et al.*, issued December 30, 1975, 1975 at column 19, lines 18-35 for examples of ampholytic surfactants. Preferred amphoteric include C_{12} -C_{18} alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C_6-C_{12} alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), C_{12}-C_{18} betaines and sulfobetaines ("sultaines"), C_{10}-C_{18} amine oxides, and mixtures thereof.

Zwitterionic surfactants can also be incorporated into the detergent compositions hereof. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. 3,929,678 Laughlin *et al.*, issued December 30, 1975 at column 19, line 38 through column 22, line 48 for examples of zwitterionic surfactants. Ampholytic and zwitterionic surfactants are generally used in combination with one or more anionic and/or nonionic surfactants.

Polyhydroxy Fatty Acid Amide Surfactant - The detergent compositions hereof may also contain an effective amount of polyhydroxy fatty acid amide surfactant. By "effective amount" is meant that the formulator of the composition can select an amount of polyhydroxy fatty acid amide to be incorporated into the compositions that will improve the cleaning performance of the detergent composition. In general, for conventional levels, the incorporation of about 1%, by weight, polyhydroxy fatty acid amide will enhance cleaning performance.

The detergent compositions herein will typically comprise about 1% weight basis, polyhydroxy fatty acid amide surfactant, preferably from about 3% to about 30%, of the polyhydroxy fatty acid amide. The polyhydroxy fatty acid amide surfactant component comprises compounds of the structural formula:

$$R^2-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle R^1}{|}}{N}-Z$$

wherein: R^1 is H, C_1-C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferably C_1-C_4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl); and R^2 is a C_5-C_{31} hydrocarbyl, preferably straight chain C_7-C_{19} alkyl or alkenyl, more preferably straight chain C_9-C_{17} alkyl or alkenyl, most preferably straight chain C_{11}-C_{15} alkyl or alkenyl, or mixtures thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z will be a glycityl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of $-CH_2-(CHOH)_n-CH_2OH$, $-CH(CH_2OH)-(CHOH)_{n-1}-CH_2OH$, $-CH_2-(CHOH)_2(CHOR')(CHOH)-CH_2OH$, and alkoxylated derivatives thereof, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide. Most preferred are glycityls wherein n is 4, particularly $-CH_2-(CHOH)_4-CH_2OH$.

R' can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl.

R^2-CO-N< can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

Z can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl, 1-deoxymaltotriotityl, etc.

Methods for making polyhydroxy fatty acid amides are known in the art. In general, they can be made by reacting an alkyl amine with a reducing sugar in a reductive amination reaction to form a corresponding N-alkyl polyhydroxyamine, and then reacting the N-alkyl polyhydroxyamine with a fatty aliphatic ester or triglyceride in a condensation/amidation step to form the N-alkyl, N-polyhydroxy fatty acid amide product. Processes for making compositions containing polyhydroxy fatty acid amides are disclosed, for example, in G.B. Patent Specification 809,060, published February 18, 1959, by Thomas Hedley & Co., Ltd., U.S. 2,965,576 Wilson, issued December 20, 1960, U.S. 2,703,798 Schwartz, issued March 8, 1955, and U.S. 1,985,424 Piggott, issued December 25, 1934 each of which is incorporated herein by reference.

Diamines

The preferred liquid detergent compositions of the present invention further comprise one or more diamines, preferably an amount of diamine such that the ratio of anionic surfactant present to the diamine is from about 40 : 1 to about 2: 1. Said diamines provide for increased removal of grease and greasy food material while maintaining suitable levels of suds.

The diamines suitable for use in the compositions of the present invention have the formula:

$$\begin{matrix} R & & & & R \\ & \diagdown & & \diagup & \\ & N & -X- & N & \\ & \diagup & & \diagdown & \\ R & & & & R \end{matrix}$$

wherein each R is independently selected from the group consisting of hydrogen, C_1-C_4 linear or branched alkyl, alkyleneoxy having the formula:

$$—(R^2O)_yR^3$$

wherein R^2 is C_2-C_4 linear or branched alkylene, and mixtures thereof; R^3 is hydrogen, C_1-C_4 alkyl, and mixtures thereof; y is from 1 to about 10; preferably at least 2 R units are hydrogen, more preferably each R unit is hydrogen; X is a backbone unit selected from:

i) C_3-C_{10} linear alkylene, C_3-C_{10} branched alkylene, C_3-C_{10} cyclic alkylene, C_3-C_{10} branched cyclic alkylene, an alkyleneoxyalkylene having the formula:

$$—(R^2O)_yR^2—$$

wherein R^2 and y are the same as defined herein above;

ii) C_3-C_{10} linear, C_3-C_{10} branched linear, C_3-C_{10} cyclic, C_3-C_{10} branched cyclic alkylene, C_6-C_{10} arylene, wherein said unit comprises one or more electron donating or electron withdrawing moieties which provide said diamine with a pK_a greater than about 8; and

iii) mixtures of (i) and (ii).

The preferred diamines of the present invention have a pK_1 and pK_2 which are each in the range of from about 8 to about 11.5, preferably in the range of from about 8.4 to about 11, more preferably from about 8.6 to about 10.75. For the purposes of the present invention the term "pK_a" stands equally well for the terms "pK_1" and "pK_2" either separately or collectively. The term pK_a as used herein throughout the present specification in the same manner as used by those of ordinary skill in the art. pK_a values are readily obtained from standard literature sources, for example, "Critical Stability

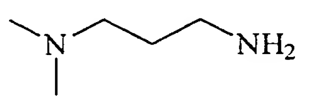
Constants: Volume 2, Amines" by Smith and Martel, Plenum Press, N.Y. and London, (1975).

As an applied definition herein, the pK_a values of the diamines are specified as being measured in an aqueous solution at 25° C having an ionic strength of from about 0.1 to about 0.5 M. As used herein, the pK_a is an equilibrium constant dependent upon temperature and ionic strength, therefore, value reported by literature references, not measured in the above described manner, may not be within full agreement with the values and ranges which comprise the present invention. To eliminate ambiguity, the relevant conditions and/or references used for pK_a's of this invention are as defined herein or in "Critical Stability Constants: Volume 2, Amines". One typical method of measurement is the potentiometric titration of the acid with sodium hydroxide and determination of the pK_a by suitable methods as described and referenced in "The Chemist's Ready Reference Handbook" by Shugar and Dean, McGraw Hill, NY, 1990.

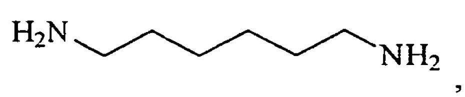
Preferred diamines for performance and supply considerations are 1,3-diaminopropane (pK_1=10.5; pK_2=8.8), 1,6-diaminohexane (pK_1=11; pK_2=10), 1,3-diaminopentane (Dytek EP) (pK_1=10.5; pK_2=8.9), 2-methyl 1,5-diaminopentane (Dytek A) (pK_1=11.2; pK_2=10.0). Other preferred materials are the primary/primary diamines having alkylene spacers ranging from C_4-C_8. In general, primary diamines are preferred over secondary and tertiary diamines.

The following are non-limiting examples of diamines suitable for use in the present invention.

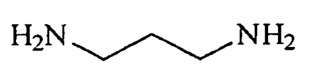
1-N,N-dimethylamino-3-aminopropane having the formula:



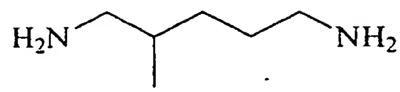
1,6-diaminohexane having the formula:



1,3-diaminopropane having the formula:



2-methyl-1,5-diaminopentane having the formula:



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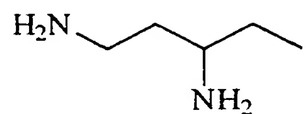
1,3-diaminopentane, available under the tradename Dytek EP, having the formula:



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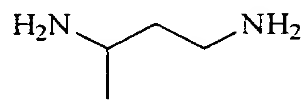
1,3-diaminobutane having the formula:



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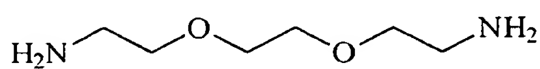
Jeffamine EDR 148, a diamine having an alkyleneoxy backbone, having the formula:



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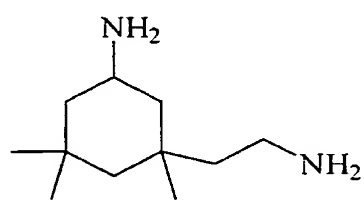
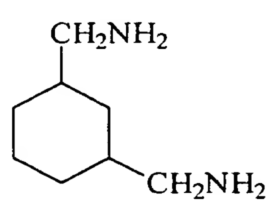
3-methyl-3-aminoethyl-5-dimethyl-1-aminocyclohexane (isophorone diamine) having the formula:



, and

1,3-bis(methylamino)cyclohexane having the formula:



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ADJUNCT INGREDIENTS

Builder - The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates and fatty acids, materials such as ethylene-diamine tetraacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylene-phosphonic acid. Though less preferred for obvious environmental reasons, phosphate builders can also be used herein.

Suitable polycarboxylates builders for use herein include citric acid, preferably in the form of a water-soluble salt, derivatives of succinic acid of the formula R-CH(COOH)CH_2(COOH) wherein R is C10-20 alkyl or alkenyl, preferably C_{12-16}, or wherein R can be substituted with hydroxyl, sulfo sulfoxyl or sulfone substituents. Specific examples include lauryl succinate , myristyl succinate, palmityl succinate 2-dodecenylsuccinate, 2-tetradecenyl succinate. Succinate builders are preferably used in the form of their water-soluble salts, including sodium, potassium, ammonium and alkanolammonium salts.

Other suitable polycarboxylates are oxodisuccinates and mixtures of tartrate monosuccinic and tartrate disuccinic acid such as described in US 4,663,071.

Especially for the liquid execution herein, suitable fatty acid builders for use herein are saturated or unsaturated C_{10-18} fatty acids, as well as the corresponding soaps. Preferred saturated species have from 12 to 16 carbon atoms in the alkyl chain. The preferred unsaturated fatty acid is oleic acid. Other preferred builder system for liquid compositions is based on dodecenyl succinic acid and citric acid.

Detergency builder salts are normally included in amounts of from 3% to 50% by weight of the composition preferably from 5% to 30% and most usually from 5% to 25% by weight.

Enzymes - Detergent compositions of the present invention may further comprise one or more enzymes which provide cleaning performance benefits. Said enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, lipases, cutinases, pectinases, xylanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, ß-glucanases, arabinosidases or mixtures thereof. A preferred combination is a detergent composition having a cocktail of conventional applicable enzymes like protease, amylase, lipase, cutinase and/or cellulase.

Cellulases - the cellulases usable in the present invention include both bacterial or fungal cellulase. Suitable cellulases are disclosed in U.S. 4,435,307, Barbesgoard *et al.*,

which discloses fungal cellulase produced from *Humicola insolens*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832.

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800. Other suitable cellulases are cellulases originated from *Humicola insolens* having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo).

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991.

Said cellulases and/or peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Proteolytic Enzyme - The proteolytic enzyme can be of animal, vegetable or microorganism (preferred) origin. The proteases for use in the detergent compositions herein include (but are not limited to) trypsin, subtilisin, chymotrypsin and elastase-type proteases. Preferred for use herein are subtilisin-type proteolytic enzymes. Particularly preferred is bacterial serine proteolytic enzyme obtained from Bacillus subtilis and/or Bacillus licheniformis.

Suitable proteolytic enzymes include Novo Industri A/S Alcalase® (preferred), Esperase®, Savinase® (Copenhagen, Denmark), Gist-brocades' Maxatase®, Maxacal® and Maxapem 15® (protein engineered Maxacal®) (Delft, Netherlands), and subtilisin BPN and BPN'(preferred), which are commercially available. Preferred proteolytic enzymes are also modified bacterial serine proteases, such as those made by Genencor International, Inc. (San Francisco, California) which are described in European Patent 251,446B, granted December 28, 1994 (particularly pages 17, 24 and 98) and which are also called herein "Protease B". U.S. 5,030,378 Venegas, issued July 9, 1991, refers to a modified bacterial serine proteolytic enzyme (Genencor International) which is called

"Protease A" herein (same as BPN'). In particular see columns 2 and 3 of U.S. 5,030,378 for a complete description, including amino sequence, of Protease A and its variants. Other proteases are sold under the tradenames: Primase, Durazym, Opticlean and Optimase. Preferred proteolytic enzymes, then, are selected from the group consisting of Alcalase ® (Novo Industri A/S), BPN', Protease A and Protease B (Genencor), and mixtures thereof. Protease B is most preferred.

Of particular interest for use herein are the proteases described in U.S. 5,470,733.

Also proteases described in our co-pending application USSN 08/136,797 can be included in the detergent composition of the invention.

Another preferred protease, referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO 95/10615 published April 20, 1995 by Genencor International (A. Baeck et al. entitled "Protease-Containing Cleaning Compositions" having U.S. Serial No. 08/322,676, filed October 13, 1994).

Useful proteases are also described in PCT publications: WO 95/30010 published November 9, 1995 by The Procter & Gamble Company; WO 95/30011 published November 9, 1995 by The Procter & Gamble Company; WO 95/29979 published November 9, 1995 by The Procter & Gamble Company.

Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Lipase - suitable lipase enzymes include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescens* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Further suitable lipases are lipases such as M1 Lipase® and Lipomax® (Gist-Brocades). Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum var. lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum*

lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. LIPOLASE® enzyme derived from *Humicola lanuginosa* and commercially available from Novo, see also EP 341,947, is a preferred lipase for use herein. Lipase and amylase variants stabilized against peroxidase enzymes are described in WO 9414951 A to Novo. See also WO 9205249 and RD 94359044.

Highly preferred lipases are the D96L lipolytic enzyme variant of the native lipase derived from *Humicola lanuginosa* as described in US Serial No. 08/341,826. (See also patent application WO 92/05249 viz. wherein the native lipase ex Humicola lanuginosa aspartic acid (D) residue at position 96 is changed to Leucine (L). According to this nomenclature said substitution of aspartic acid to Leucine in position 96 is shown as : D96L.) Preferably the *Humicola lanuginosa* strain DSM 4106 is used.

In spite of the large number of publications on lipase enzymes, only the lipase derived from *Humicola lanuginosa* and produced in *Aspergillus oryzae* as host has so far found widespread application as additive for washing products. It is available from Novo Nordisk under the tradename Lipolase® and Lipolase Ultra®, as noted above. In order to optimize the stain removal performance of Lipolase, Novo Nordisk have made a number of variants. As described in WO 92/05249, the D96L variant of the native *Humicola lanuginosa* lipase improves the lard stain removal efficiency by a factor 4.4 over the wild-type lipase (enzymes compared in an amount ranging from 0.075 to 2.5 mg protein per liter). Research Disclosure No. 35944 published on March 10, 1994, by Novo Nordisk discloses that the lipase variant (D96L) may be added in an amount corresponding to 0.001-100- mg (5-500,000 LU/liter) lipase variant per liter of wash liquor.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor).

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Amylase - Amylases (α and/or ß) can be included for removal of carbohydrate-based stains. Suitable amylases are Termamyl® (Novo Nordisk), Fungamyl® and BAN® (Novo Nordisk). The enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Amylase enzymes are normally incorporated in the detergent composition at levels from 0.0001% to 2%, preferably from about 0.0001% to about 0.5%, more preferably from about 0.0005% to about 0.1%, even more

preferably from about 0.001% to about 0.05% of active enzyme by weight of the detergent composition.

Amylase enzymes also include those described in WO95/26397 and in co-pending application by Novo Nordisk PCT/DK96/00056. Other specific amylase enzymes for use in the detergent compositions of the present invention therefore include :

(a) α-amylases characterized by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas ® α-amylase activity assay. Such Phadebas® α-amylase activity assay is described at pages 9-10, WO95/26397.

(b) α-amylases according (a) comprising the amino sequence shown in the SEQ ID listings in the above cited reference. or an α-amylase being at least 80% homologous with the amino acid sequence shown in the SEQ ID listing.

(c) α-amylases according (a) obtained from an alkalophilic *Bacillus* species, comprising the following amino sequence in the N-terminal : His-His-Asn-Gly-Thr-Asn-Gly-Thr-Met-Met-Gln-Tyr-Phe-Glu-Trp-Tyr-Leu-Pro-Asn-Asp.

    A polypeptide is considered to be X% homologous to the parent amylase if a comparison of the respective amino acid sequences, performed via algorithms, such as the one described by Lipman and Pearson in Science 227, 1985, p. 1435, reveals an identity of X%

(d) α-amylases according (a-c) wherein the α-amylase is obtainable from an alkalophilic Bacillus species; and in particular, from any of the strains NCIB 12289, NCIB 12512, NCIB 12513 and DSM 935.

    In the context of the present invention, the term "obtainable from" is intended not only to indicate an amylase produced by a Bacillus strain but also an amylase encoded by a DNA sequence isolated from such a Bacillus strain and produced in an host organism transformed with said DNA sequence.

(e) α-amylase showing positive immunological cross-reactivity with antibodies raised against an α-amylase having an amino acid sequence corresponding respectively to those α-amylases in (a-d).

(f) Variants of the following parent α-amylases which (i) have one of the amino acid sequences shown in corresponding respectively to those α-amylases in (a-e), or (ii) displays at least 80% homology with one or more

of said amino acid sequences, and/or displays immunological cross-reactivity with an antibody raised against an α-amylase having one of said amino acid sequences, and/or is encoded by a DNA sequence which hybridizes with the same probe as a DNA sequence encoding an α-amylase having one of said amino acid sequence; in which variants :

1. at least one amino acid residue of said parent α-amylase has been deleted; and/or
2 at least one amino acid residue of said parent α-amylase has been replaced by a different amino acid residue; and/or
3. at least one amino acid residue has been inserted relative to said parent α-amylase; said variant having an α-amylase activity and exhibiting at least one of the following properties relative to said parent α-amylase : increased thermostability, increased stability towards oxidation, reduced Ca ion dependency, increased stability and/or α-amylolytic activity at neutral to relatively high pH values, increased α-amylolytic activity at relatively high temperature and increase or decrease of the isoelectric point (pI) so as to better match the pI value for α-amylase variant to the pH of the medium.

Said variants are described in the patent application PCT/DK96/00056.

Other amylases suitable herein include, for example, α-amylases described in GB 1,296,839 to Novo; RAPIDASE®, International Bio-Synthetics, Inc. and TERMAMYL®, Novo. FUNGAMYL® from Novo is especially useful. Engineering of enzymes for improved stability, e.g., oxidative stability, is known. See, for example J. Biological Chem., Vol. 260, No. 11, June 1985, pp. 6518-6521. Certain preferred embodiments of the present compositions can make use of amylases having improved stability in detergents such as automatic dishwashing types, especially improved oxidative stability as measured against a reference-point of TERMAMYL® in commercial use in 1993. These preferred amylases herein share the characteristic of being "stability-enhanced" amylases, characterized, at a minimum, by a measurable improvement in one or more of: oxidative stability, e.g., to hydrogen peroxide/tetraacetylethylenediamine in buffered solution at pH 9-10; thermal stability, e.g., at common wash temperatures such as about 60°C; or alkaline stability, e.g., at a pH from about 8 to about 11, measured versus the above-identified reference-point amylase. Stability can be measured using any of the art-disclosed technical tests. See, for example, references disclosed in WO 9402597. Stability-enhanced amylases can be obtained from

Novo or from Genencor International. One class of highly preferred amylases herein have the commonality of being derived using site-directed mutagenesis from one or more of the *Bacillus* amylases, especially the *Bacillus* α-amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors. Oxidative stability-enhanced amylases vs. the above-identified reference amylase are preferred for use, especially in bleaching, more preferably oxygen bleaching, as distinct from chlorine bleaching, detergent compositions herein. Such preferred amylases include (a) an amylase according to the hereinbefore incorporated WO 9402597, Novo, Feb. 3, 1994, as further illustrated by a mutant in which substitution is made, using alanine or threonine, preferably threonine, of the methionine residue located in position 197 of the *B. licheniformis* alpha-amylase, known as TERMAMYL®, or the homologous position variation of a similar parent amylase, such as *B. amyloliquefaciens, B. subtilis,* or *B. stearothermophilus;* (b) stability-enhanced amylases as described by Genencor International in a paper entitled "Oxidatively Resistant alpha-Amylases" presented at the 207th American Chemical Society National Meeting, March 13-17 1994, by C. Mitchinson. Therein it was noted that bleaches in automatic dishwashing detergents inactivate alpha-amylases but that improved oxidative stability amylases have been made by Genencor from *B. licheniformis* NCIB8061. Methionine (Met) was identified as the most likely residue to be modified. Met was substituted, one at a time, in positions 8, 15, 197, 256, 304, 366 and 438 leading to specific mutants, particularly important being M197L and M197T with the M197T variant being the most stable expressed variant. Stability was measured in CASCADE® and SUNLIGHT®; (c) particularly preferred amylases herein include amylase variants having additional modification in the immediate parent as described in WO 9510603 A and are available from the assignee, Novo, as DURAMYL®. Other particularly preferred oxidative stability enhanced amylase include those described in WO 9418314 to Genencor International and WO 9402597 to Novo. Any other oxidative stability-enhanced amylase can be used, for example as derived by site-directed mutagenesis from known chimeric, hybrid or simple mutant parent forms of available amylases. Other preferred enzyme modifications are accessible. See WO 9509909 A to Novo.

Enzyme Stabilizing System - The enzyme-containing compositions herein may optionally also comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the detersive enzyme. Such a system may be inherently provided by other formulation actives, or be added separately, e.g., by the formulator or

by a manufacturer of detergent-ready enzymes. Such stabilizing systems can, for example, comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, and mixtures thereof, and are designed to address different stabilization problems depending on the type and physical form of the detergent composition.

One stabilizing approach is the use of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. Calcium ions are generally more effective than magnesium ions and are preferred herein if only one type of cation is being used. Typical detergent compositions, especially liquids, will comprise from about 1 to about 30, preferably from about 2 to about 20, more preferably from about 8 to about 12 millimoles of calcium ion per liter of finished detergent composition, though variation is possible depending on factors including the multiplicity, type and levels of enzymes incorporated. Preferably water-soluble calcium or magnesium salts are employed, including for example calcium chloride, calcium hydroxide, calcium formate, calcium malate, calcium maleate, calcium hydroxide and calcium acetate; more generally, calcium sulfate or magnesium salts corresponding to the exemplified calcium salts may be used. Further increased levels of Calcium and/or Magnesium may of course be useful, for example for promoting the grease-cutting action of certain types of surfactant.

Another stabilizing approach is by use of borate species. See Severson, U.S. 4,537,706. Borate stabilizers, when used, may be at levels of up to 10% or more of the composition though more typically, levels of up to about 3% by weight of boric acid or other borate compounds such as borax or orthoborate are suitable for liquid detergent use. Substituted boric acids such as phenylboronic acid, butaneboronic acid, p-bromophenylboronic acid or the like can be used in place of boric acid and reduced levels of total boron in detergent compositions may be possible though the use of such substituted boron derivatives.

Stabilizing systems of certain cleaning compositions, for example automatic dishwashing compositions, may further comprise from 0 to about 10%, preferably from about 0.01% to about 6% by weight, of chlorine bleach scavengers, added to prevent chlorine bleach species present in many water supplies from attacking and inactivating the enzymes, especially under alkaline conditions. While chlorine levels in water may be small, typically in the range from about 0.5 ppm to about 1.75 ppm, the available chlorine in the total volume of water that comes in contact with the enzyme, for example during dish- or fabric-washing, can be relatively large; accordingly, enzyme stability to chlorine in-use is sometimes problematic. Since perborate or percarbonate, which have

the ability to react with chlorine bleach, may present in certain of the instant compositions in amounts accounted for separately from the stabilizing system, the use of additional stabilizers against chlorine, may, most generally, not be essential, though improved results may be obtainable from their use. Suitable chlorine scavenger anions are widely known and readily available, and, if used, can be salts containing ammonium cations with sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetraacetic acid (EDTA) or alkali metal salt thereof, monoethanolamine (MEA), and mixtures thereof can likewise be used. Likewise, special enzyme inhibition systems can be incorporated such that different enzymes have maximum compatibility. Other conventional scavengers such as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc., and mixtures thereof can be used if desired. In general, since the chlorine scavenger function can be performed by ingredients separately listed under better recognized functions, (e.g., hydrogen peroxide sources), there is no absolute requirement to add a separate chlorine scavenger unless a compound performing that function to the desired extent is absent from an enzyme-containing embodiment of the invention; even then, the scavenger is added only for optimum results. Moreover, the formulator will exercise a chemist's normal skill in avoiding the use of any enzyme scavenger or stabilizer which is majorly incompatible, as formulated, with other reactive ingredients. In relation to the use of ammonium salts, such salts can be simply admixed with the detergent composition but are prone to adsorb water and/or liberate ammonia during storage. Accordingly, such materials, if present, are desirably protected in a particle such as that described in US 4,652,392, Baginski *et al.*

Perfumes - Perfumes and perfumery ingredients useful in the present compositions and processes comprise a wide variety of natural and synthetic chemical ingredients, including, but not limited to, aldehydes, ketones, esters, and the like. Also included are various natural extracts and essences which can comprise complex mixtures of ingredients, such as orange oil, lemon oil, rose extract, lavender, musk, patchouli, balsamic essence, sandalwood oil, pine oil, cedar, and the like. Finished perfumes can comprise extremely complex mixtures of such ingredients. Finished perfumes typically comprise from about 0.01% to about 2%, by weight, of the detergent compositions herein, and individual perfumery ingredients can comprise from about 0.0001% to about 90% of a finished perfume composition.

Non-limiting examples of perfume ingredients useful herein include: 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl naphthalene; ionone methyl; ionone gamma methyl; methyl cedrylone; methyl dihydrojasmonate; methyl 1,6,10-trimethyl-2,5,9-cyclododecatrien-1-yl ketone; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; 4-acetyl-6-tert-butyl-1,1-dimethyl indane; para-hydroxy-phenyl-butanone; benzophenone; methyl beta-naphthyl ketone; 6-acetyl-1,1,2,3,3,5-hexamethyl indane; 5-acetyl-3-isopropyl-1,1,2,6-tetramethyl indane; 1-dodecanal, 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde; 7-hydroxy-3,7-dimethyl ocatanal; 10-undecen-1-al; iso-hexenyl cyclohexyl carboxaldehyde; formyl tricyclodecane; condensation products of hydroxycitronellal and methyl anthranilate, condensation products of hydroxycitronellal and indol, condensation products of phenyl acetaldehyde and indol; 2-methyl-3-(para-tert-butylphenyl)-propionaldehyde; ethyl vanillin; heliotropin; hexyl cinnamic aldehyde; amyl cinnamic aldehyde; 2-methyl-2-(para-iso-propylphenyl)-propionaldehyde; coumarin; decalactone gamma; cyclopentadecanolide; 16-hydroxy-9-hexadecenoic acid lactone; 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-gamma-2-benzopyrane; beta-naphthol methyl ether; ambroxane; dodecahydro-3a,6,6,9a-tetramethyl-naphtho[2,1b]furan; cedrol, 5-(2,2,3-trimethylcyclopent-3-enyl)-3-methylpentan-2-ol; 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol; caryophyllene alcohol; tricyclodecenyl propionate; tricyclodecenyl acetate; benzyl salicylate; cedryl acetate; and para-(tert-butyl) cyclohexyl acetate.

Particularly preferred perfume materials are those that provide the largest odor improvements in finished product compositions containing cellulases. These perfumes include but are not limited to: hexyl cinnamic aldehyde; 2-methyl-3-(para-tert-butylphenyl)-propionaldehyde; 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl naphthalene; benzyl salicylate; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; para-tert-butyl cyclohexyl acetate; methyl dihydro jasmonate; beta-napthol methyl ether; methyl beta-naphthyl ketone; 2-methyl-2-(para-iso-propylphenyl)-propionaldehyde; 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-gamma-2-benzopyrane; dodecahydro-3a,6,6,9a-tetramethylnaphtho[2,1b]furan; anisaldehyde; coumarin; cedrol; vanillin; cyclopentadecanolide; tricyclodecenyl acetate; and tricyclodecenyl propionate.

Other perfume materials include essential oils, resinoids, and resins from a variety of sources including, but not limited to: Peru balsam, Olibanum resinoid, styrax, labdanum resin, nutmeg, cassia oil, benzoin resin, coriander and lavandin. Still other perfume chemicals include phenyl ethyl alcohol, terpineol, linalool, linalyl acetate, geraniol, nerol, 2-(1,1-dimethylethyl)-cyclohexanol acetate, benzyl acetate, and eugenol. Carriers such as diethylphthalate can be used in the finished perfume compositions.

Polymeric Dispersing Agents - Polymeric dispersing agents can advantageously be utilized at levels from about 0.1% to about 7%, by weight, in the compositions herein. It is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent performance by crystal growth inhibition, particulate soil release peptization, and anti-redeposition.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued march 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such

materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Other polymeric materials which can be included are polypropylene glycol (PPG), propylene glycol (PG), and polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

Additionally, polymeric soil release agents, hereinafter "SRA" or "SRA's", can optionally be employed in the present detergent compositions. If utilized, SRA's will generally comprise from 0.01% to 10.0%, typically from 0.1% to 5%, preferably from 0.2% to 3.0% by weight, of the composition.

Preferred SRA's typically have hydrophilic segments to hydrophilize the surface of hydrophobic fibers such as polyester and nylon, and hydrophobic segments to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles thereby serving as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with SRA to be more easily cleaned in later washing procedures.

SRA's can include a variety of charged, e.g., anionic or even cationic (see U.S. 4,956,447), as well as noncharged monomer units and structures may be linear, branched or even star-shaped. They may include capping moieties which are especially effective in controlling molecular weight or altering the physical or surface-active properties. Structures and charge distributions may be tailored for application to different fiber or textile types and for varied detergent or detergent additive products.

Preferred SRA's include oligomeric terephthalate esters, typically prepared by processes involving at least one transesterification/oligomerization, often with a metal catalyst such as a titanium(IV) alkoxide. Such esters may be made using additional monomers capable of being incorporated into the ester structure through one, two, three, four or more positions, without of course forming a densely crosslinked overall structure.

Suitable SRA's include products as described in U.S. 4,968,451; U.S. 4,711,730; U.S. 4,721,580; U.S. 4,702,857; U.S. 4,877,896; U.S. 3,959,230; U.S. 3,893,929; U. S. 4,000,093; EP Appl. 0 219 048; U.S. 5,415,807; U.S. 4,201,824; U.S. 4,240,918; U.S. 4,525,524; U.S. 4,201,824; U.S. 4,579,681; EP 279,134A; EP 457,205; DE 2,335,044; U.S. 4,240,918; U. S. 4,787,989; U. S. 4,525,524; U.S. 4,877,896; U.S. 4,968,451; U.S. 4,702,857; U.S. Appl. 08/545,351; and U.S. Appl. 08/355,938. Commercially available examples include SOKALAN HP-22, available from BASF, Germany; ZELCON 5126 from Dupont; and MILEASE T from ICI.

Alkoxylated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq., incorporated herein by reference. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula $-(CH_2CH_2O)_m(CH_2)_nCH_3$ wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxylated polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

Another polymer dispersant form use herein includes polyethoxyated-polyamine polymers (PPP). The preferred polyethoxylated-polyamines useful herein are generally polyalkyleneamines (PAA's), polyalkyleneimines (PAI's), preferably polyethyleneamine (PEA's), polyethyleneimines (PEI's). A common polyalkyleneamine (PAA) is tetrabutylenepentamine. PEA's are obtained by reactions involving ammonia and ethylene dichloride, followed by fractional distillation. The common PEA's obtained are triethylenetetramine (TETA) and teraethylenepentamine (TEPA). Above the pentamines, i.e., the hexamines, heptamines, octamines and possibly nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See U.S. 2,792,372 Dickinson, issued May 14, 1957, which describes the preparation of PEA's.

Polyamines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing these polyamine backbones are disclosed in U.S. 2,182,306 Ulrich *et al.*, issued December 5, 1939; U.S. 3,033,746 Mayle *et al.*, issued May 8, 1962; U.S. 2,208,095 Esselmann *et al.*,

issued July 16, 1940; U.S. 2,806,839 Crowther, issued September 17, 1957; and U.S. 2,553,696 Wilson, issued May 21, 1951; all herein incorporated by reference.

Additionally, certain alkoxylated (especially ethoxylated) quaternary polyamine dispersants are useful herein as dispersants. The alkoxylated quaternary polyamine dispersants which can be used in the present invention are of the general formula:

$$R_1-\overset{\displaystyle A}{\underset{\displaystyle A}{\overset{|}{\underset{|}{N^{\oplus}}}}}-R-\left[\overset{\displaystyle A}{\underset{\displaystyle R_1}{\overset{|}{\underset{|}{N^{\oplus}}}}}-R\right]_m-\overset{\displaystyle A}{\underset{\displaystyle A}{\overset{|}{\underset{|}{N^{\oplus}}}}}-R_1 \qquad (m+2)\,X^{\ominus}$$

where R is selected from linear or branched C_2-C_{12} alkylene, C_3-C_{12} hydroxyalkylene, C_4-C_{12} dihydroxyalkylene, C_8-C_{12} dialkylarylene, $[(CH_2CH_2O)_qCH_2CH_2]$- and -$CH_2CH(OH)CH_2O$-$(CH_2CH_2O)_qCH_2CH(OH)CH_2]$- where q is from about 1 to about 100. If present, Each R_1 is independently selected from C_1-C_4 alkyl, C_7-C_{12} alkylaryl, or A. R_1 may be absent on some nitrogens; however, at least three nitrogens must be quaternized. A has the formula:

$$(\underset{\displaystyle R^3}{\underset{|}{C}}HCH_2O)_nB$$

where R^3 is selected from H or C_1-C_3 alkyl, n is from about 5 to about 100 and B is selected from H, C_1-C_4 alkyl, acetyl, or benzoyl; m is from about 0 to about 4, and X is a water soluble anion.

In preferred embodiments, R is selected from C_4 to C_8 alkylene, R_1 is selected from C_1-C_2 alkyl or C_2-C_3 hydroxyalkyl, and A is:

$$(\underset{\displaystyle R^3}{\underset{|}{C}}HCH_2O)_nH$$

where R_3 is selected from H or methyl, and n is from about 10 to about 50; and m is 1.

In another preferred embodiment R is linear or branched C_6, R_1 is methyl, R_3 is H, and n is from about 20 to about 50, and m is 1.

The levels of these dispersants used can range from about 0.1% to about 10%, typically from about 0.4% to about 5%, by weight. These dispersants can be synthesized following the methods outline in US. 4,664,848, or other ways known to those skilled in the art.

<u>Brightener</u> - Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.01% to about 1.2%,

by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. 4,790,856 Wixon, issued December 13, 1988. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic White CWD, the 2-(4-styryl-phenyl)-2H-naptho[1,2-d]triazoles; 4,4'-bis-(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)bisphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl- amino coumarin; 1,2-bis(benzimidazol-2-yl)ethylene; 1,3-diphenyl-pyrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-styryl-naptho[1,2-d]oxazole; and 2-(stilben-4-yl)-2H-naphtho[1,2-d]triazole. See also U.S. Patent 3,646,015, issued February 29, 1972 to Hamilton.

Chelating Agents - The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilo-tri-acetates, ethylenediamine tetrapro-prionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at lease low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. 3,812,044 Connor *et al.*, issued May 21, 1974. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. 4,704,233 Hartman *et al.*, issued November 3, 1987.

The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder. Similarly, the so called "weak" builders such as citrate can also be used as chelating agents.

If utilized, these chelating agents will generally comprise from about 0.1% to about 15% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Composition pH

Dishwashing compositions of the invention will be subjected to acidic stresses created by food soils when put to use, i.e., diluted and applied to soiled dishes. If a composition with a pH greater than 7 is to be more effective, it preferably should contain a buffering agent capable of providing a generally more alkaline pH in the composition and in dilute solutions, i.e., about 0.1% to 0.4% by weight aqueous solution, of the composition. The pKa value of this buffering agent should be about 0.5 to 1.0 pH units below the desired pH value of the composition (determined as described above). Preferably, the pKa of the buffering agent should be from about 7 to about 10. Under these conditions the buffering agent most effectively controls the pH while using the least amount thereof.

The buffering agent may be an active detergent in its own right, or it may be a low molecular weight, organic or inorganic material that is used in this composition solely for maintaining an alkaline pH. Preferred buffering agents for compositions of this invention are nitrogen-containing materials. Some examples are amino acids such as lysine or lower alcohol amines like mono-, di-, and tri-ethanolamine. Other preferred nitrogen-containing buffering agents are Tris(hydroxymethyl)amino methane $(HOCH_2)_3CNH_3$ (TRIS), 2-amino-2-ethyl-1,3-propanediol, 2-amino-2-methyl-propanol, 2-amino-2-methyl-1,3-propanol, disodium glutamate, N-methyl diethanolamide, 1,3-diamino-propanol N,N'-tetra-methyl-1,3-diamino-2-propanol, N,N-bis(2-hydroxyethyl)glycine (bicine) and N-tris (hydroxymethyl)methyl glycine (tricine). Mixtures of any of the above are also acceptable. Useful inorganic buffers/alkalinity

sources include the alkali metal carbonates and alkali metal phosphates, e.g., sodium carbonate, sodium polyphosphate. For additional buffers see McCutcheon's EMULSIFIERS AND DETERGENTS, North American Edition, 1997, McCutcheon Division, MC Publishing Company Kirk and WO 95/07971 both of which are incorporated herein by reference.

The buffering agent, if used, is present in the compositions of the invention herein at a level of from about 0.1% to 15%, preferably from about 1% to 10%, most preferably from about 2% to 8%, by weight of the composition.

Other Ingredients - A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, hydrotropes, antioxidants, processing aids, dyes or pigments, solvents for liquid formulations, solid fillers for bar compositions, etc. If high sudsing is desired, suds boosters such as the C_{10}-C_{16} alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C_{10}-C_{14} monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous.

An antioxidant can be optionally added to the detergent compositions of the present invention. They can be any conventional antioxidant used in detergent compositions, such as 2,6-di-tert-butyl-4-methylphenol (BHT), carbamate, ascorbate, thiosulfate, monoethanolamine(MEA), dietahanolamine, triethanolamine, etc. It is preferred that the antioxidant, when present, be present in the composition from about 0.001% to about 5% by weight.

Various detersive ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the detersive ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the detersive ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended detersive function.

To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3%-5% of C_{13-15} ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the

aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents, including liquid laundry detergent compositions.

Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to about 6 carbon atoms and from 2 to about 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

An example of the procedure for making granules of the detergent compositions herein is as follows: - Linear aklylbenzenesulfonate, sodium tripolyphosphate, sodium silicate, sodium sulfate perfume, diamine and water are added to, heated and mixed via a crutcher. The resulting slurry is spray dried into a granular form.

An example of the procedure for making liquid detergent compositions herein is as follows: - To the free water, citrate and $MgCl_2$ are added and dissolved. To this solution amine oxide, betaine, ethanol, hydrotrope and nonionic surfactant are added. If free water isn't available, the $MgCl_2$ and citrate are added to the above mix then stirred until dissolved. At this point, maleic acid is added then followed by the diamine. AExS is added last. In formulations without Mg^{++} the procedure is the same.

Non-Aqueous Liquid Detergents

The manufacture of liquid detergent compositions which comprise a non-aqueous carrier medium can be prepared according to the disclosures of U.S. Patents 4,753,570; 4,767,558; 4,772,413; 4,889,652; 4,892,673; GB-A-2,158,838; GB-A-2,195,125; GB-A-2,195,649; U.S. 4,988,462; U.S. 5,266,233; EP-A-225,654 (6/16/87); EP-A-510,762 (10/28/92); EP-A-540,089 (5/5/93); EP-A-540,090 (5/5/93); U.S. 4,615,820; EP-A-565,017 (10/13/93); EP-A-030,096 (6/10/81), incorporated herein by reference. Such compositions can contain various particulate detersive ingredients (e.g., bleaching agents, as disclosed hereinabove) stably suspended therein. Such non-aqueous compositions thus comprise a LIQUID PHASE and, optionally but preferably, a SOLID PHASE, all as described in more detail hereinafter and in the cited references.

The compositions of this invention can be used to form aqueous washing solutions for use hand dishwashing. Generally, an effective amount of such compositions is added to water to form such aqueous cleaning or soaking solutions. The aqueous solution so formed is then contacted with the dishware, tableware, and cooking utensils.

An effective amount of the detergent compositions herein added to water to form aqueous cleaning solutions can comprise amounts sufficient to form from about 500 to 20,000 ppm of composition in aqueous solution. More preferably, from about 800 to 5,000 ppm of the detergent compositions herein will be provided in aqueous cleaning liquor.

The present invention also relates to a means for preventing the redeposition of grease, oils, and dirt, especially grease, from the hand washing solution onto dishware. This method comprises contacting an aqueous solution of the compositions of the present invention with soiled dishware and washing said dishware with said aqueous solution.

An effective amount of the detergent compositions herein added to water to form aqueous cleaning solutions according to the method of the present invention comprises amounts sufficient to form from about 500 to 20,000 ppm of composition in aqueous solution. More preferably, from about 800 to 5,000 ppm of the detergent compositions herein will be provided in aqueous cleaning liquor.

The liquid detergent compositions of the present invention are effective for preventing the redeposition of grease from the wash solution back onto the dishware during washing. One measure of effectiveness of the compositions of the present invention involves redeposition tests. The following test and others of similar nature are used to evaluate the suitability of the formulas described herein.

A polyethylene 2 L graduated cylinder is filled to the 1 L graduation mark with an aqueous (water = 7 grain) solution comprising from about 500 to about 20,000 ppm of a liquid detergent composition according to the present invention. A synthetic greasy soil composition is then added to the cylinder and the solution is agitated. After a period of time the solution is decanted from the graduated cylinder and the interior walls of the graduated cylinder are rinsed with a suitable solvent or combination of solvents to recover any re-deposited greasy soil. The solvent is removed and the weight of greasy soil which remains in solution is determined by subtracting the amount of soil recovered from the amount initially added to the aqueous solution.

Other re-deposition test include immersion of tableware, flatware, and the like and recovering any re-deposited soil.

The above test can be further modified to determine the increased amount of suds volume and suds duration. The solution is first agitated then subsequently challenged with portions of greasy soil with agitation between each subsequent soil addition. The suds volume can be easily determined by using the vacant volume of the 2 L cylinder as a guide.

The following are non-limiting examples of liquid detergent compositions comprising the polymeric suds extenders according to the present invention.

TABLE I

weight %

Ingredients	1	2	3
C_{12}-C_{15} Alkyl sulphate	--	28.0	25.0
C_{12}-C_{13} Alkyl ($E_{0.6-3}$) sulfate	30	--	--
C_{12} Amine oxide	5.0	3.0	7.0
C_{12}-C_{14} Betaine	3.0	--	1.0
C_{12}-C_{14} Polyhydroxy fatty acid amide	--	1.5	--
C_{10} Alcohol Ethoxylate E_9 [1]	2.0	--	4.0
Diamine [2]	1.0	--	7.0
Mg^{2+} (as $MgCl_2$)	0.25	--	--
Citrate (cit2K3)	0.25	--	--
Polymeric suds booster [3]	1.25	2.6	0.9
Minors and water [4]	balance	balance	balance
pH of a 10% aqueous solution	9	10	10

1. E_9 Ethoxylated Alcohols as sold by the Shell Oil Co.
2. 1,3-diaminopentane sold as Dytek EP.
3. Polypeptide comprising Lys, Ala, Glu, Tyr (5:6:2:1) having a molecular weight of approximately 52,000 daltons.
4. Includes perfumes, dyes, ethanol, etc.

TABLE II

weight %

Ingredients	4	5	6
C_{12}-C_{13} Alkyl ($E_{0.6-3}$) sulfate	--	15.0	10.0
Paraffin sulfonate	20.0	--	--
Na C_{12}-C_{13} linear alkylbenzene sulfonate	5.0	15.0	12.0
C_{12}-C_{14} Betaine	3.0	1.0	--
C_{12}-C_{14} Polyhydroxy fatty acid amide	3.0	--	1.0
C_{10} Alcohol Ethoxylate E_9 [1]	--	--	20.0
Diamine [2]	1.0	-	7.0

DTPA [3]	--	0.2	--
Mg^{2+} (as $MgCl_2$)	1.0	--	--
Ca^{2+} (as $Ca(citrate)_2$)	--	0.5	--
Protease [4]	0.01	--	0.05
Amylase [5]	--	0.05	0.05
Hydrotrope [6]	2.0	1.5	3.0
Polymeric suds booster [7]	0.5	3.0	0.5
Minors and water [8]	balance	balance	balance
pH of a 10% aqueous solution	9.3	8.5	11

1. E_9 Ethoxylated Alcohols as sold by the Shell Oil Co.
2. 1,3-bis(methylamino)cyclohexane.
3. Diethylenetriaminepentaacetate.
4. Suitable protease enzymes include Savinase®; Maxatase®; Maxacal®; Maxapem 15®; subtilisin BPN and BPN'; Protease B; Protease A; Protease D; Primase®; Durazym®; Opticlean®;and Optimase®; and Alcalase ®.
5. Suitable amylase enzymes include Termamyl®, Fungamyl®; Duramyl®; BAN®, and the amylases as described in WO95/26397 and in co-pending application by Novo Nordisk PCT/DK/96/00056.
6. Suitable hydrotropes include sodium, potassium, ammonium or water-soluble substituted ammonium salts of toluene sulfonic acid, naphthalene sulfonic acid, cumene sulfonic acid, xylene sulfonic acid.
7. Polypeptide comprising Lys, Ala, Glu, Tyr (5:6:2:1) having a molecular weight of approximately 52,000 daltons.
8. Includes perfumes, dyes, ethanol, etc.

TABLE III

weight %

Ingredients	**7**	**8**	**9**	**10**
C_{12}-C_{15} Alkyl (E_1) sulfate	--	30.0	--	--
C_{12}-C_{15} Alkyl ($E_{1.4}$) sulfate	30.0	--	27.0	--
C_{12}-C_{15} Alkyl ($E_{2.2}$) sulfate	--	--	--	15
C_{12} Amine oxide	5.0	5.0	5.0	3.0
C_{12}-C_{14} Betaine	3.0	3.0	--	--
C_{10} Alcohol Ethoxylate E_9 [1]	2.0	2.0	2.0	2.0
Diamine [2]	1.0	2.0	4.0	2.0

Mg^{2+} (as $MgCl_2$)	0.25	0.25	--	--
Ca^{2+} (as Ca(citrate)$_2$)	--	0.4	--	--
Polymeric suds booster [3]	0.5	1.0	0.75	5.0
Minors and water [4]	balance	balance	balance	balance
pH of a 10% aqueous solution	7.4	7.6	7.4	7.8

1. E_9 Ethoxylated Alcohols as sold by the Shell Oil Co.
2. 1,3-bis(methylamino)cyclohexane.
3. Polypeptide comprising Lys, Ala, Glu, Tyr (5:6:2:1) having a molecular weight of approximately 52,000 daltons.
4. Includes perfumes, dyes, ethanol, etc.

TABLE IV

weight %

Ingredients	**11**	**12**	**13**
C_{12}-C_{13} Alkyl ($E_{0.6-3}$) sulfate	--	15.0	10.0
Paraffin sulfonate	20.0	--	--
Na C_{12}-C_{13} linear alkylbenzene sulfonate	5.0	15.0	12.0
C_{12}-C_{14} Betaine	3.0	1.0	--
C_{12}-C_{14} Polyhydroxy fatty acid amide	3.0	--	1.0
C_{10} Alcohol Ethoxylate E_9 [1]	--	--	20.0
Diamine [2]	1.0	--	7.0
Mg^{2+} (as $MgCl_2$)	1.0	--	--
Ca^{2+} (as Ca(citrate)$_2$)	--	0.5	--
Protease [3]	0.1	--	--
Amylase [4]	--	0.02	--
Lipase [5]	--	--	0.025
DTPA [6]	--	0.3	--
Citrate (cit2K3)	0.65	--	--
Polymeric suds booster [7]	1.5	2.2	3.0
Minors and water [8]	balance	balance	balance
pH of a 10% aqueous solution	9.3	8.5	11

1. E_9 Ethoxylated Alcohols as sold by the Shell Oil Co.
2. 1,3-diaminopentane sold as Dytek EP.

3. Suitable protease enzymes include Savinase®; Maxatase®; Maxacal®; Maxapem 15®; subtilisin BPN and BPN'; Protease B; Protease A; Protease D; Primase®; Durazym®; Opticlean®;and Optimase®; and Alcalase ®.
4. Suitable amylase enzymes include Termamyl®, Fungamyl®; Duramyl®; BAN®, and the amylases as described in WO95/26397 and in co-pending application by Novo Nordisk PCT/DK/96/00056.
5. Suitable lipase enzymes include Amano-P; M1 Lipase®; Lipomax®; Lipolase®; D96L - lipolytic enzyme variant of the native lipase derived from *Humicola lanuginosa* as described in US Patent Application Serial No. 08/341,826; and the *Humicola lanuginosa* strain DSM 4106
6. Diethylenetriaminepentaacetate.
7. Lysozyme.
8. Includes perfumes, dyes, ethanol, etc.

TABLE V

weight %

Ingredients	14	15	16
C_{12}-C_{13} Alkyl ($E_{0.6-3}$) sulfate	--	27.0	--
C_{12}-C_{14} Betaine	2.0	2.0	--
C_{14} Amine oxide	2.0	5.0	7.0
C_{12}-C_{14} Polyhydroxy fatty acid amide	2.0	--	--
C_{10} Alcohol Ethoxylate E_9 [1]	1.0	--	2.0
Hydrotrope	--	--	5.0
Diamine [2]	4.0	2.0	5.0
Ca^{2+} (as $Ca(citrate)_2$)	--	0.1	0.1
Protease [3]	--	0.06	0.1
Amylase [4]	0.005	--	0.05
Lipase [5]	--	0.05	--
DTPA [6]	--	0.1	0.1
Citrate (cit2K3)	0.3	--	--
Polymeric suds booster [7]	0.5	0.8	2.5
Minors and water [8]	balance	balance	balance
pH of a 10% aqueous solution	10	9	9.2

1. E_9 Ethoxylated Alcohols as sold by the Shell Oil Co.
2. 1,3-bis(methylamino)cyclohexane.

3. Suitable protease enzymes include Savinase®; Maxatase®; Maxacal®; Maxapem 15®; subtilisin BPN and BPN'; Protease B; Protease A; Protease D; Primase®; Durazym®; Opticlean®;and Optimase®; and Alcalase ®.
4. Suitable amylase enzymes include Termamyl®, Fungamyl®; Duramyl®; BAN®, and the amylases as described in WO95/26397 and in co-pending application by Novo Nordisk PCT/DK/96/00056.
5. Suitable lipase enzymes include Amano-P; M1 Lipase®; Lipomax®; Lipolase®; D96L - lipolytic enzyme variant of the native lipase derived from *Humicola lanuginosa* as described in US Patent Application Serial No. 08/341,826; and the *Humicola lanuginosa* strain DSM 4106
6. Diethylenetriaminepentaacetate.
7. Polypeptide comprising Lys, Ala, Glu, Tyr (5:6:2:1) having a molecular weight of approximately 52,000 daltons.
8. Includes perfumes, dyes, ethanol, etc.

TABLE VI

	weight %		
Ingredients	**17**	**18**	**19**
C_{12}-C_{13} Alkyl ($E_{1.4}$) sulfate	33.29	24.0	--
C_{12}-C_{13} Alkyl ($E_{0.6}$) sulfate	--	--	26.26
C_{12}-C_{14} Polyhydroxy fatty acid amide	4.2	3.0	1.37
C_{14} Amine oxide	4.8	2.0	1.73
C_{11} Alcohol Ethoxylate E_9 [1]	1.0	4.0	4.56
C_{12}-C_{14} Betaine	--	2.0	1.73
$MgCl_2$	0.72	0.47	0.46
Calcium citrate	0.35	--	--
Polymeric suds booster [2]	0.5	1.0	2.0
Minors and water [3]	balance	balance	balance
pH of a 10% aqueous solution	7.4	7.8	7.8

1. E_9 Ethoxylated Alcohols as sold by the Shell Oil Co.
2. Polypeptide comprising Lys, Ala, Glu, Tyr (5:6:2:1) having a molecular weight of approximately 52,000 daltons.
3. Includes perfumes, dyes, ethanol, etc.

What is claimed is:

1. A detergent composition suitable for use in hand dishwashing, said composition comprising:
   a) an effective amount of a proteinaceous suds stabilizer, said stabilizer having an isoelectric point of from 9 to 11.5;
   b) an effective amount of a detersive surfactant; and
   c) the balance carriers and other adjunct ingredients;

   provided the pH of a 10% aqueous solution of said composition is from 7 to 12.

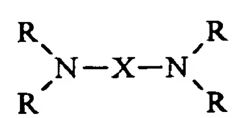
2. A composition according to Claim 1 comprising from 0.5% to 5% by weight, of said proteinaceous suds stabilizer.

3. A composition according to any of Claims 1-2 wherein said proteinaceous suds stabilizer is a peptide comprising from 10% to 40% of one or more amino acids which are protonated at a pH of less than 11.

4. A composition according to any of Claims 1-3 wherein said proteinaceous suds stabilizer comprises at least 10% by weight, of one or more amino acids.

5. A composition according to any of Claims 1-2 and 4 wherein said proteinaceous suds stabilizer comprises at least 10% by weight of one or more amino acids which are protonated at a pH of less than 11.

6. A composition according to any of Claims 1-5 further comprising from 0.25% to 15% of a diamine wherein said diamine has the formula:



wherein each R is independently selected from the group consisting of hydrogen, C_1-C_4 linear or branched alkyl, alkyleneoxy having the formula:

$$—(R^2O)_yR^3$$

wherein R^2 is C_2-C_4 linear or branched alkylene, and mixtures thereof; R^3 is hydrogen, C_1-C_4 alkyl, and mixtures thereof; y is from 1 to 10; X is a unit selected from:

i) C_3-C_{10} linear alkylene, C_3-C_{10} branched alkylene, C_3-C_{10} cyclic alkylene, C_3-C_{10} branched cyclic alkylene, an alkyleneoxyalkylene having the formula:

$$—(R^2O)_yR^2—$$

wherein R^2 and y are the same as defined herein above;

ii) C_3-C_{10} linear, C_3-C_{10} branched linear, C_3-C_{10} cyclic, C_3-C_{10} branched cyclic alkylene, C_6-C_{10} arylene, wherein said unit comprises one or more electron donating or electron withdrawing moieties which provide said diamine with a pK_a greater than 8; and

iii) mixtures of (i) and (ii)

provided said diamine has a pK_a of at least 8.

7. A composition according to any of Claims 1-6 further comprising an enzyme selected from the group consisting of proteases, amylases, lipases, cellulases and mixtures thereof.

8. A proteinaceous suds stabilizer comprising at least 10% by weight of amino acid residues wherein said suds stabilizer having an isoelectric point of from 9.5 to 11.5 and a molecular weight of at least 1500 daltons.

9. A compound according to Claim 8 comprising at least 10% by weight of units having the formula:

$$—NH—(CH_2)_x—\underset{R^1}{\overset{R}{C}}—(CH_2)_y—\overset{O}{\overset{\|}{C}}—$$

wherein R and R^1 are each independently hydrogen, a moiety having a positive charge or negative charge at a pH of from 9.5 to 11.5, x and y are each independently 0 or 1.

10. A compound according to any of Claims 8-9 comprising greater than 95% by weight, of amino acids.

INTERNA[redacted]L SEARCH REPORT

Inte[redacted]al Application No
PC[redacted]S 98/24707

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/37 C11D3/30 C11D3/00 C11D3/384

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 116 568 A (COLGATE-PALMOLIVE) 28 September 1983 see page 1, paragraph 1 see page 2, paragraph 3-5 see page 6, line 17 - page 7, line 19; claims 1,2,14,16,17 ---	1,2,8
X	FR 2 208 972 A (PROCTER & GAMBLE) 28 June 1974 see claim 1 ---	1,2,8
X	FR 2 208 978 A (PROCTER & GAMBLE) 28 June 1974 see claim 1 ---	1,2,8
X	FR 2 198 992 A (PROCTER & GAMBLE) 5 April 1974 see claim 1 ---	1,2,8
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 March 1999	22/03/1999

Name and mailing address of the ISA	Authorized officer
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International Application No
PCT/US 98/24707

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